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A COMPARATIVE STUDY OF THE LIGHT SENSIBILITY
OF
SELENIUM AND STIBNITE AT 20°C. AND -190°C.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY
IN CONFORMITY WITH THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY.

BY

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JUNE
1914.

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A Comparative Study of the Light Sensibility of Selenium and Stibnite at 20° C. and - 190° C.

It has been known for some time that selenium exists in three distinct modifications, and it is also known that this element experiences a decrease in resistance when exposed to light under proper conditions. Correlating these two facts, a number of investigators have adopted the following explanation of the light sensitiveness of selenium. They assumed that in the light-sensitive variety all three modifications exist in equilibrium. The effect of illumination is to disturb this equilibrium and to cause an intertransformation in favor of that particular modification which conducts electricity most easily. This theory may be called the chemical theory, and on this basis, we should expect the sensibility of selenium to accord with well known chemical facts.

It was suggested by Pfund [1] that the conduction in selenium is electronic and that the sensibility may be accounted for on the assumption that the light in falling on the selenium is absorbed. By this process electrons are set in resonance, resulting in an expulsion of electrons outside the atoms. This would increase the number available for carrying the current.

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[1] Phys. Rev. 28, 1909, p. 324.

Among the facts that can be marshalled in support of this electronic hypothesis, the most important are these:

1. As shown by Thomson in his "Conduction of Electricity through Gases", the current through a gas ionized by photo-electric action is proportional to the square root of the energy of the exciting light, provided the ionization has reached a steady state. The same law has been shown by Pfund[1] and Nicholson[2] to hold for selenium for unlimited exposures to visible radiations and X-rays.

2. Another general property of electronic conduction is the absence of polarization. A number of investigators [3] have definitely established the fact that normal selenium cells show no polarization.

3. The retention of light-sensibility at the temperature of liquid air is also evidence for the electronic hypothesis. This property of selenium is clearly shown by the experiments of Pochettino[4], Miss McDowell[5] and the author.

4. All light sensitive substances show the "voltage effects";

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[1] Pfund. Phys. Rev. XXXIV, No. 5, May, 1912

[2] Nicholson. Phys. Rev. Vol. III, Jan. 1914.

[3] Ries. "Electrical Properties of Selenium p. 53;
Pfund. Phys. Zeit. 10, 340, 1909.

[4] Pochettino. Rend. R. Accad. dei Linc. Sec. 5, vol. II, p. 286.

[5] McDowell. Phys. Rev. 31, p. 524, 1910.

i.e. Ohm's law is not obeyed. Ries[1], Adams[2] and Luterbacher[3] have shown for selenium, that the specific resistance decreases with the voltage, and for the same voltage also decreases with time.

Object of Investigation:

As the information on selenium at liquid air temperatures was not as complete as might be desired, it seemed advisable to investigate this further. The particular object of the investigation, however, was to examine other light sensitive substances and determine whether or not they showed behavior similar to selenium at 20° C. and - 190° C. Due to lack of time, most of the observations have been confined to stibnite whose light sensitive properties were discovered by Jaeger[4].

Cells:-

In order to carry out this investigation, it was first necessary to prepare cells which would meet the exorbitant demands necessitated by this temperature variation. It soon became evident that selenium cells prepared in the usual way would not suffice, as it was found that after a cell had been subjected to the temperature

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[1] Ries. Phys. Zeit. 12, p. 480 & 552, 1911.
[2] Adams. Proc. Roy. Soc. 23, 1875.
[3] Luterbacher. Ann d. Phys. 33, 1392, 1910.
[4] Jaeger. Proc. Roy. Acad. Sci. Amsterdam, 9, 808, 1907.

of liquid air and brought back to 20°, its behavior was markedly different.

After some experimenting, cells were finally constructed according to the following design. This cell has proven so satisfactory that it seems well to describe it in some detail.

Selenium Cells:- Amorphous selenium was first cast into discs about 1.5 cm. in diameter and 1.5 mm. thick. These were sensitized in the usual way, being maintained at a temperature of 200° C. for six hours and then cooled rapidly to room temperature. The discs were then ground down smooth on crocus cloth; and silver tape electrodes were fastened on with celluloid. A film of gold was next deposited by cathode sputtering; and finally, the gold was removed along a narrow line [illegible] a [illegible] as shown in the drawing. Attention is called to the four shallow pools of celluloid shown. Besides strengthening the construction these provided a smooth transition from the selenium to the upper surface of the silver tape. In this way fractures of the gold film were avoided. The time required for this deposition, from the insertion of the cell until its removal did not exceed 20 minutes, but as a matter of fact, the selenium was covered with a protective layer of gold within six minutes. No evidence of any deleterious

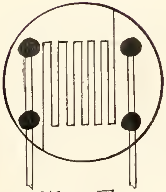

Fig. I

action due to mercury vapor could be detected., The cell was finally enclosed in a glass tube similar in design to Fig. II .

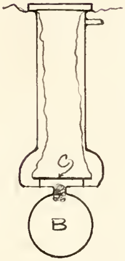

Fig. II

Bulb B was filled with calcium chloride and the constriction leading to the upper chamber loosely plugged with cotton. The cell c was fastened with sealing wax in this upper chamber, the end of which was closed by a glass plate. The vessel was also provided with a side tube for exhausting by means of an aspirator, a phosphorous pentoxide tube being inserted between cell and aspirator during the process.

Stibnite Cells. Stibnite cells were made and mounted in essentially the same way as the selenium cells. Starting out with crystals of stibnite (Sb_2S_3) and using the cleavage surfaces, in some cases gold was deposited over the whole surface and afterwards removed along a line by scratching; in other cases, a protective layer about .5 mm. wide was placed along the middle of the crystal before deposition. This strip was afterwards removed disclosing a strip of clean stibnite cleavage surface which could be exposed to light.

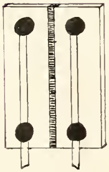

Fig. III

Oxides. Oxides of iron, nickel and copper were formed by heating the pure metals in an electric furnace. These were equipped with electrodes and mounted like selenium and stibnite. Cells of Molybdenite were also prepared.

Apparatus: The arrangement of apparatus is shown in Fig. IV. The source of illumination was a Nernst lamp L; a spectrometer of the Wadsworth type broke up the radiation into quasi-monochromatic light focussed in the plane of slit S_2; the light could then follow one of two paths depending upon whether the right angle prism P, hinged at H was raised or lowered. With the prism P swung out of the way, the light was focussed by lens L_2 on a sensitive thermal junction. This system constructed according to his latest design[1], together with a sensitive galvanometer, was built by Pfund and kindly placed at my disposal. Its sensibility was such that a candle at a meter's distance gave a deflection of 30 mm. With the prism P down, the light was diverted downward upon the cell c which was inserted in a Dewar flask. The amount of glass in the path of the beam over both paths was approximately the same; and it might be said at this point that in carrying out any set of experiments to determine the effect of voltage or temperature or of anything else, these factors could be varied without disturbing the cell in any way. Results obtained are therefore strictly comparable.

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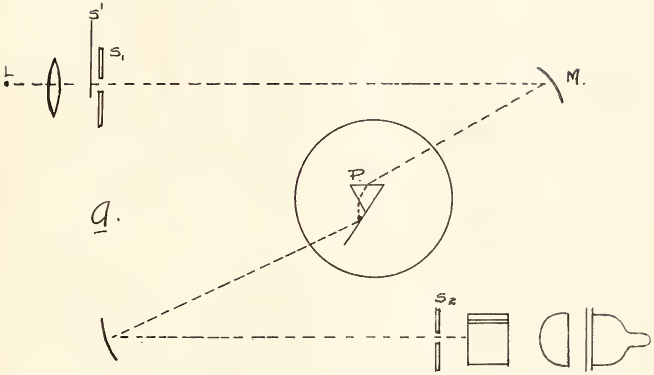
[1] Phys. Zeit. XIII, 870, 1912.

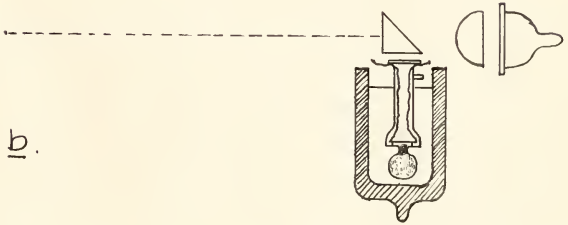
Figure. IV

a - Plan

b - Elevation.



a.



b.

In measuring increased conductivity the usual method was employed. A diagram shows the arrangement. In some cases a counter e.m.f. was introduced at the galvanometer terminals to annul the "dark deflections"; and, when the increased conductivity was too large, a shunt R_3 was introduced to cut down this deflection. In some cases both counter e.m.f. and shunt were unnecessary. Both this galvanometer (sensibility 1.5 x 10^{-8} amp.) and a device for exposing for the desired time were placed in an adjoining room. In general, exposures of ten seconds were taken, and an interval of three or four minutes elapsed between readings.

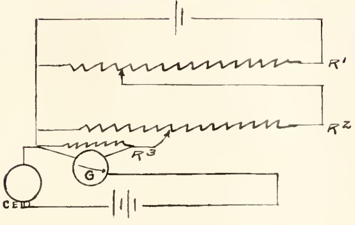


Figure V

Sensibility Curves at 20°C. and - 190° C. Selenium 20° C.

In these observations selenium cells of the previously mentioned type were used. Both the counter e.m.f. and shunt had to be employed, and observations were taken on a number of cells.

Strictly speaking, the "sensibility" of a cell is the ratio of the two quantities, - the change in resistance per unit energy illumination and the "dark resistance." The quantity used in these curves is proportional to the sensibility. What was actually done was as follows: The galvanometer deflection corresponding to a certain

value of the incident energy was first obtained. The deflection corresponding to a particular value of energy taken as unity could then be calculated from the relation $D = K E^{\beta}$, where D is the galvanometer deflection, K a constant, E the incident energy and β another constant. Pfund and Nicholson have shown that $\beta = .5$, and this value was used in applying the formula unless definitely stated otherwise.

A specimen set of observations on cell Selenium D, resistance 775,000 ohms is given below. Column (1) gives the wave-length; columns (2) and (3) the energy and galvanometer deflections respectively; column (4) the galvanometer deflection corresponding to unit energy, calculated from relation $D = K E^{\beta}$. 100 mm. was taken as unit energy deflection. Column (5) gives $\underline{\Delta C}$ which could be calculated from column (4) from a knowledge of the shunt employed. Since the resistance of the cell remained approximately constant throughout a set of readings, $\underline{\Delta c}$ is proportional to the sensibility. It is to be observed from Table I, that actual observations near the sensibility maximum were taken for energies which do not vary appreciably from that value of energy taken as standard. This was accomplished by adjusting the voltage on the Nernst lamp and the width of the slit S. In this way all possibility of vitiation of the results by the assumption of any law connecting galvanometer deflections and energy was obviated.

Table I.

Selenium Cell D. 110 Volts.

Temperature 23.5

Wave-length	Energy defl. mm.	Galv. defl.	Galv. defl. calc. for E=100	ΔC
.495 μ	8	.5mm.	1.77 mm.	29.65
.520	17	1.0	2.42	40.54
.550	25	1.8	3.6	60.3
.580	47	5.5	8.02	134.3
.620	90	9.0	9.49	158.9
.632	97	12.0	12.18	204.0
.655	109	23.0	22.03	369.0
.670	103	35.0	34.49	577.7
.689	101.5	47.0	46.65	781.0
.710	110.5	54.5	51.85	868.5
.735	102.5	44.0	43.54	729.3
.762	106.0	29.5	28.00	469.0
.800	101.5	18.0	17.86	299.15
.837	96.0	15.5	15.82	265.0
.895	98.0	12.[illegible]	12.12	203.00
.982	104.0	8.0	7.85	131.5
1.08	101.0	3.5	3.48	58.29
1.38	100.0	.5	.5	8.38

Each one of the observations in columns (2) and (3) represent the mean of at least two readings, and these do not differ appreciably from one another. The results of this table are plotted in Curve I.

Sensibility Curve of Selenium at - 190°C.

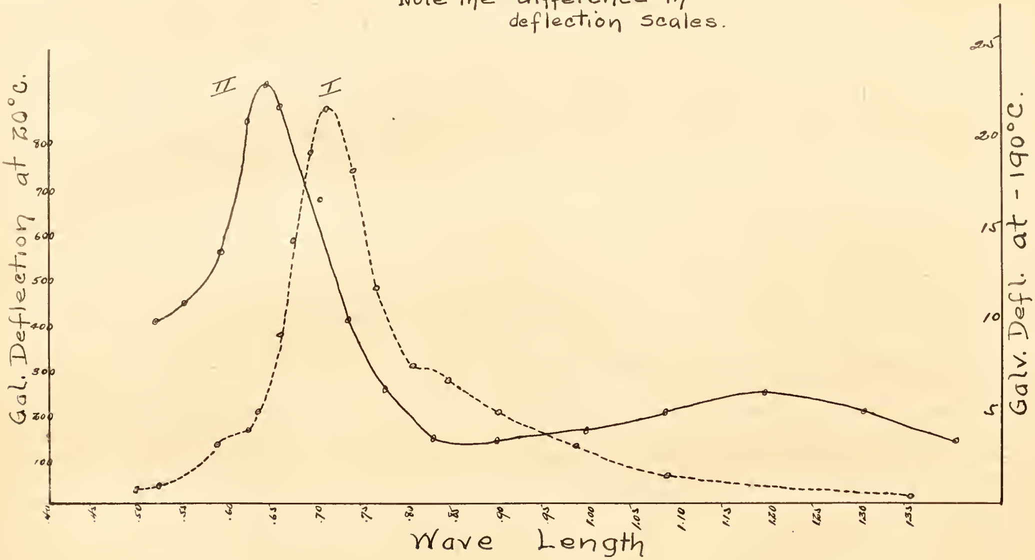
In taking these curves the Dewar flask was filled with liquid air and replaced about the cell. This adjustment could be effected without disturbing the rest of the apparatus. Sufficient care was taken to see that the flask remained well filled with liquid air. By means of a funnel arrangement, not shown in the drawing, the supply

— Selenium —

I. { 20° C
120 Volts
10 Sec. Exposure.

II { -190° C
120 Volts.
10 Sec. Exposure.

Note the difference in deflection scales.



could be replenished without withdrawing the flask, so that the cell remained in the liquid air throughout the experiment.

In all recorded experiments, the cell was brought to this low temperature very gradually, and throughout the procedure, the conductivity was observed to fall quite rapidly until it became barely perceptible. Observations of Pochettino[1] and McDowell[2] also show that the resistance of selenium at liquid air temperature is enormously great. In taking readings at these low temperatures, it was found that after exposure the cell returned to its original conductivity more slowly than at room temperature. The surprising thing is that the light seems to become effective just as rapidly at this low temperature as at ordinary temperatures. The deflections, of course, are enormously increased. Some other experiments, carried out in this laboratory to determine whether the number of electrons liberated was independent of the temperature, show that the effect of the light is produced within .2 sec. It seems difficult to the writer to reconcile these observations with any chemical explanation, as it is generally known that ordinary chemical processes, if they take place at all, do so with small velocities at the temperature of liquid air.

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[1] Pochettino. Rend. R. Accad. dei Linc. Ser.5, Vol. II, p. 286

[2] McDowell. Phys. Rev. 31, p. 524, 1910.

Table II.

Selenium Cell. Temperature - 190°C. Exposure 10 sec.

120 Volts. Storage Battery used.

Wave-length	Energy defl.	Galv. Defl.	Δc_1 calc. E =100mm, β=.5	Δc_2 calc. E=100mm. β=1
.520 μ	10 mm.	1 mm.	3.16 mm.	10 mm.
.550	18	2	4.71	11
.580	37	5	8.20	13.5
.620	75	15.5	17.9	20.7
.632	96	22.0	22.45	22.9
.655	103	22.5	22.17	21.8
.665	101	21.75	21.64	21.5
.678	105	24.0	23.42	22.9
.700	95	16.0	16.42	16.8
.710	93	15.5	16.07	16.7
.730	100	10.0	10.0	10.0
.762	101	8.0	7.96	7.92
.825	100	3.5	3.5	3.5
.895	106	3.75	3.65	3.54
.825	100	3.5	3.5	3.5
.895	106	4.0	3.89	3.95
.982	100	4.0	4.0	4.0
1.08	100	5.0	5.0	5.0
1.19	101	6.0	5.97	5.95
1.348	100	5.1	5.1	5.1
1.620	99	1.5	1.5	1.5
1.920	104	0	0	0
1.08	95	6.0	6.16	6.1
.762	102	6.0	5.94	5.88
.730	99	10.25	10.15	10.36
.700	101	18.0	17.91	17.82
.678	101	23.5	23.38	23.27
.655	96	29.5	30.0	30.73
.632	94	30.0	30.94	31.92
.620	80	22.0	24.6	27.50
.580	47	8.8	12.84	18:72
.520	11	1.5	4.5	13.64

The results of these observations are plotted in Curve 2. In making all observations at liquid air temperature, the cell was afterwards brought back to room temperature to determine whether or not the first readings could be reproduced. This is the reason why early observations on cells of standard designs had to be discarded as worthless. With the new design of cell no difficulty was experienced. Voltage effects were detected at liquid air temperature.

From a comparison of Curves 1 and 2 the following conclusions seem to stand out most pronounced:

The effects of low temperature are:

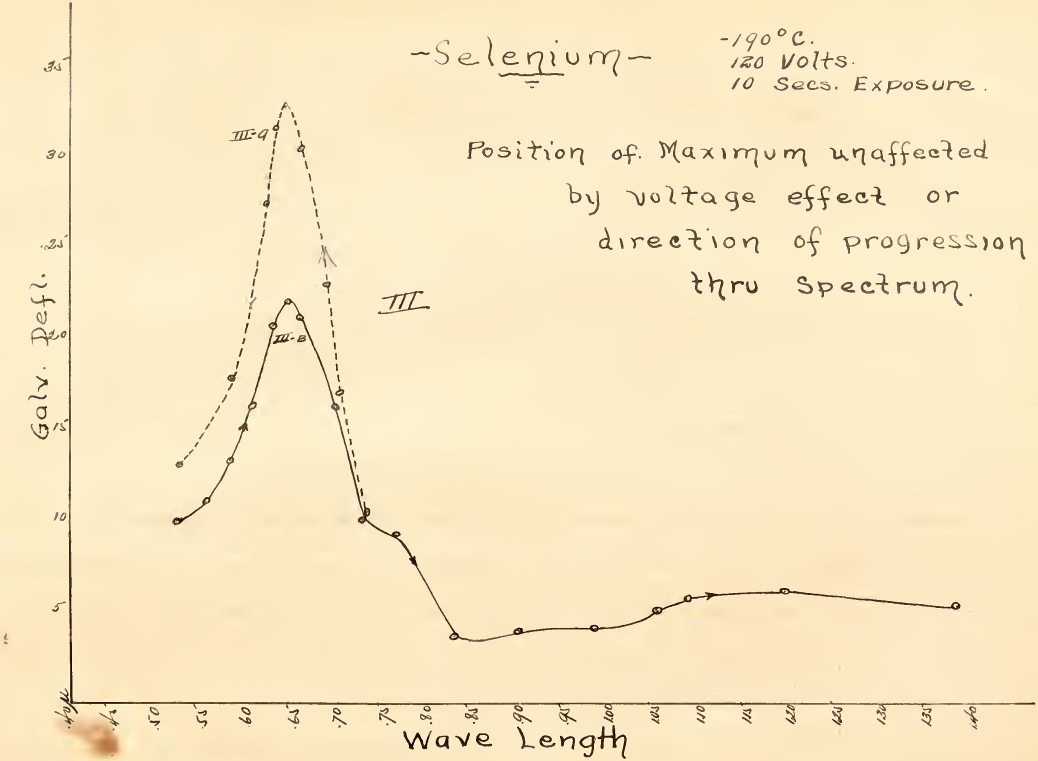
1. An extension of the range of sensibility from .9μ to 2 μ approximately.

2. A shift of the sensibility maximum to the region of shorter wavelengths by about 600 A.U.

Position of Sensibility maximum unaffected by voltage effect and direction of progression through spectrum:-

Although it seemed probable that the position of the maximum was unaffected by these factors, it was deemed best to verify this experimentally. Curves 3_a and 3_b were plotted for selenium at - 190°C.

Curve 3_a as indicated by the arrow, is plotted for readings taken through the spectrum from shorter to longer wave-lengths; Curve 3_b refers to the same cell, readings being taken in the reverse order.



-Selenium-

-190°C.
120 Volts.
10 Secs. Exposure.

Position of Maximum unaffected by voltage effect or direction of progression thru Spectrum.

During the course of these readings, the conductivity was observed to increase appreciably although the temperature must have remained constant. The curves show, however, that the sensibility maximum is unaffected by this voltage effect.

Stibnite.

The light sensitive property of stibnite ($Sb_2 S_3$) was discovered by Jaeger[1] 1907, and Ries[2] showed later that this substance exhibits the same voltage effects found in Selenium. It was decided to investigate this substance further using as the mode of attack a study of the sensibility curves obtained under various conditions.

As previously mentioned two kinds of cells were prepared from Stibnite crystals. In one type of cell the surface exposed to the light was a fresh cleavage surface which had been protected from the gold during the deposition. In the second variety gold was first deposited over the whole surface and afterwards removed along a line by scratching with a fine needle. In all cases the cells were mounted in the same manner as the Selenium cells previously described.

Law connecting Energy and Deflections. Room Temperature.

In investigating this point a rotating sector was placed before the spectrometer slit S_1 (see Fig.). The disc was so constructed that by sliding the motor along a pair of ways, full, one-half or a quarter energy was allowed to fall on the slit. The procedure was to get the galvanometer deflection for various values of the incident

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[1] Jaeger. Proc. Roy. Acad. Sci., Amsterdam. 9, 808, 1907.
[2] Ries

energy[*]

Table: III gives the results for Stibnite Cell "A".

Exposure 10 sec. 110 volts. 21° C.

Wave-lengths	D_1=galv. defl. full energy	D_2=galv.defl. 1/2 energy	D_3=galc.defl. 1/4energy	β calc from D_1&D_2	β calc. from D_1&D_3
.642 μ	9 mm.	6.2 mm.	4 mm.	.54	.58
.670	16	11	7.7	.54	.53
.685	27.5	19.3	13.7	.51	.53
.700	59	39	26.7	.59	.57
.740	137.5	95.1	66.7	.53	.52
.768	86.75	54.5	35.8	.67	.64
.800	39.5	23	15.1	.78	.69
.873	7	3	2	1.02	.92

It will be observed that the value of β for the longer wave-lengths is in general greater than for the shorter wave-lengths. This is similar to what we find in Selenium. The obvious explanation is that a greater time is required for equilibrium for the longer wave-lengths. For the same reason the value of β for all wave-lengths is too large. For exposures sufficiently long enough to ensure equilibrium it is safe to say that the square root law applies to Stibnite. In other words Stibnite obeys the law $D = KE^{\beta}$, where D is the galvanometer deflection, E is the energy and $\beta = .5$.

Sensibility Curves for Stibnite at Room Temperature.

Two specimen sensibility curves will be given in this connection. Both refer to the same cell, "Stibnite A", which had a scratched surface. The first observations were taken by exposing the cell until equilibrium was reached. Owing to the "voltage effect" in Stibnite the galvanometer never came absolutely to rest, but equilibrium was

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[*] Exposures of ten seconds were made, and the relation $D = K E^{\beta}$ was assumed to hold between galvanometer deflections and energy. Having two values of D as well as the ratio of the corresponding energies the value of β was easily calculated.

considered to be reached when the galvanometer did not move 1 mm. per minute. After each reading the cell was allowed to soak back approximately to its original conductivity before the next reading was taken. Intervals between readings amounted in some cases to as much as thirty-five minutes. The value of β was also investigated.

Table IV gives the results.

Stibnite Cell "A." 120 Volts. Battery. Temperature 20° C.

Wave-length	Energy Defl.	D_1 = galv.defl. full energy	D_2 = galv.defl. 1/2 energy	Δc calc.for E=100mm β=.5	β calc.from D_1 and d_2 assuming $D=KE^{\beta}$ (law)
.538 μ	7.5 mm.	.5		1.3mm.	
.568	14.5	2.5	1.7	6.6	.55
.584	20.	9.1	6.3	20.35	.53
.604	27.2	16.65	12	31.92	.47
.614	33.4	22	14.5	38.7	.60
.626	39.4	22	16	35.05	.46
.632	44.1	26	19.5	39.15	.42
.640	53	30.5	21.5	41.89	.50
.692	94.7	90.	59	92.48	.61
.705	67.5	98	62	119.3	.66
.740	64.9	115	73	142.75	.66
.768	75.0	93	64.5	107.4	.55
.809	100.4	24.4	17.5	24.3	.50
				Mean β	.54

β for the longer wave-length has a smaller value than for the determinations taken with a ten second exposure, the mean value for range of spectrum covered being about .54. Curve IV is plotted from these readings.

Table V refers to the same cell, readings being taken for exposures of ten seconds. All other conditions were practically the same.

Table V.

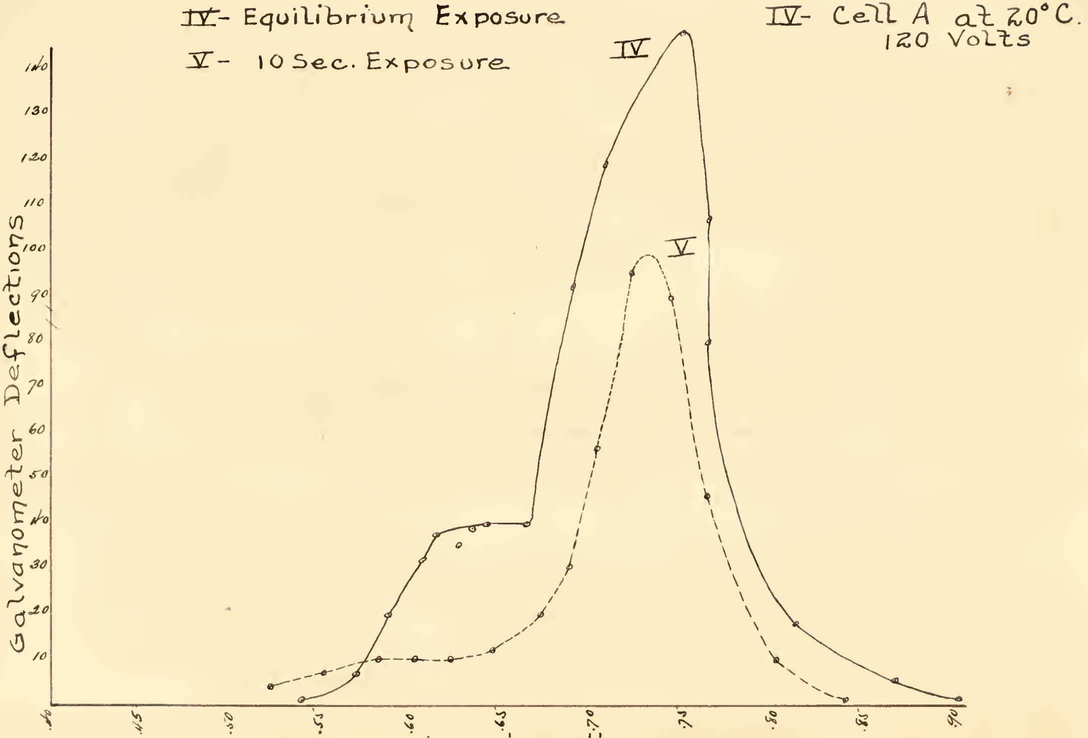
Stibnite Cell "A" Temperature 21°C.

120 Volts. 10 sec. Exposure.

Wave-lengths	Energy Defl.	Galv. Defl.	Δc calc. for E =100 mm. β =.5
.520 μ	18 mm.	2	4.71
.550	37	4	6.58
.580	65	8	9.92
.620	100	10	10.
.642	99	12	12.06
.670	105	20.5	20.00
.685	106	31	30.11
.700	100	56.5	56.5
.720	104	97	95.13
.740	103	90.5	89.16
.762	100	46.3	46.3
.800	98	10	10.10
.837	95	1.5	1.54
.895	97	.5	.51

The resulting sensibility curve is Curve V . Comparing this with CurveIV, we see that for unlimited exposures the maximum sensibility lies further in the red. The obvious explanation is that while equilibrium is approximately reached for the shorter wave-lengths in ten seconds, such is not the case for the other end of the spectrum. The effect of longer exposures is therefore to increase the ordinates corresponding to longer wave-lengths, leaving the shorter wave-lengths practically unaffected. Consequently the maximum shifts towards longer wave-lengths.

— Stibnite —


IV- Equilibrium Exposure
V- 10 Sec. Exposure
IV- Cell A at 20°C.
120 Volts
IV
V
Galvanometer Deflections
140
130
120
110
100
90
80
70
60
50
40
30
20
10
.40
.45
.50
.55
.60
.65
.70
.75
.80
.85
.90

Effect of Voltage on the Sensibility Maximum:-

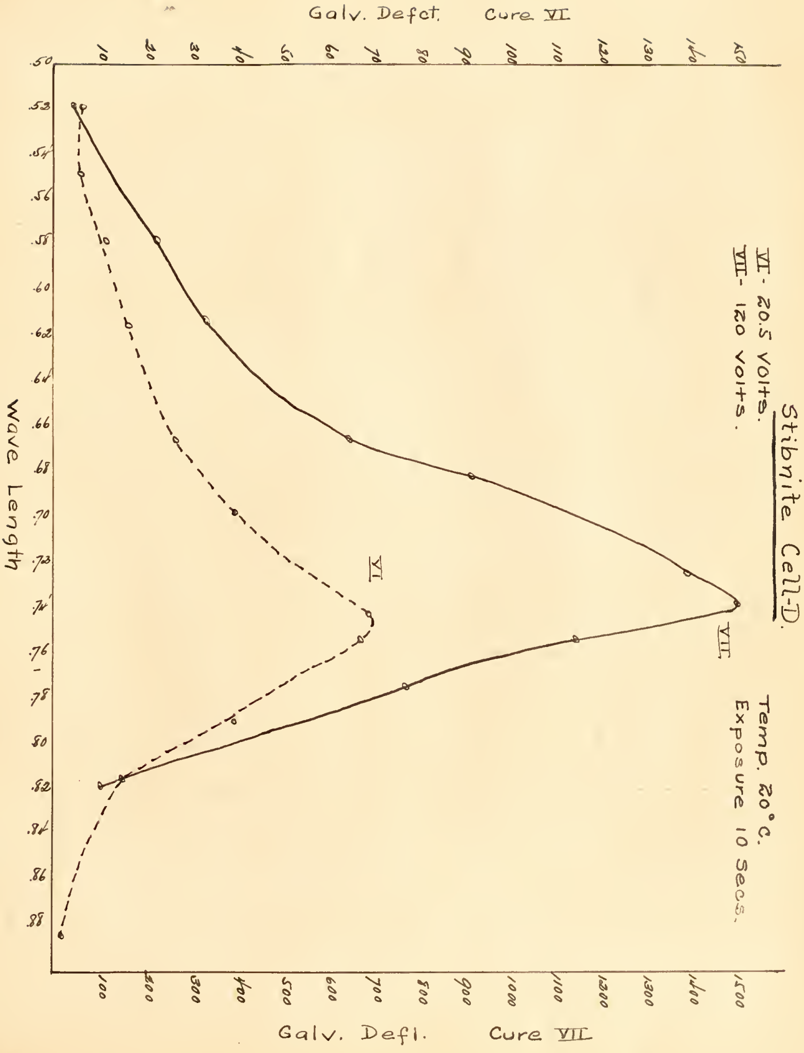
It seemed also desirable to examine the effect of voltage on the sensibility maximum. Tables VI and VII give the sensibility data for the same cell Stibnite "D" for two different voltages. In Stibnite "D" the exposed surface was one of the cleavage planes of the crystal. The resistance of this cell was somewhat lower than cell Stibnite "A".

Table VI.

Stibnite Cell "D".
Temperature 20°.5 C.

Voltage 20.5
Exposure 10 secs.

Wave-lengths	Energy Defl.	Galv. Defl.	Δc calc. F = 100 mm. β=.5
.5185 μ	7.25 mm.	1.5 mm.	5.57
.5482	13	2.3	6.38
.5782	22.25	5.8	12.3
.6176	38.9	10.4	16.67
.6670	40.7	17.3	27.12
.682	42	21	32.40
.724	57.3	42.5	56.15
.739	62.2	52	65.94
.7554	75.25	58.7	67.67
.791	88	37	39.44
.8175	76.75	14.5	14.74
.8846	111.25	2	1.9


Stibnite Cell-D.
VI - 20.5 Volts.
VII - 120 Volts.
Temp. 20° C.
Exposure 10 Secs.
Galv. Defct. Cure VI
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Galv. Defl. Cure VII
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Wave Length
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.82
.84
.86
.88
VI
VII

Table VII.

Stibnite Cell "D" Voltage 120.

Temperature 20°.5 C. Exposure 10 secs.

Wave-lengths	Energy Defl.	D_1 Galv.Defl.	D_2=Galv.Defl. calc. E=100 mm. β=.5	Δc calc. knowing shunt
.5185μ	11 mm.	1.75mm.	5.28	55.45
.5482	19	4.88	11.19	117.50
.5782	36.2	12.8	21.76	228.43
.6176	66.25	26.2	32.19	338.00
.667	94.1	59.6	61.44	645.20
.682	102.75	88.6	87.41	917.8
.724	102.4	134	132.41	1390
.739	99	142	142.72	1498.33
.7554	103	110	108.38	1137.5
.8175	100.75	8	8	103.34
.8846	97.7	No defl.		

A comparison of Curves VI and VII shows an apparent shift of the maximum towards the shorter wave-lengths for the higher voltage. While this apparent shift amounts to about 100 A.U., the author is inclined to attribute it to accidental errors. Owing to a lack of time, it was deemed inadvisable to repeat the readings at this time. This will be done in the near future.

Voltage Effects:

As other investigators[1] have already observed Stibnite shows the voltage effect. The specific resistence decreases with

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[1] Ries. Ann. d. Phys. 36, 1655, 1911.

the voltage. It is also observed that for a given voltage the conductivity decreased with time. Like Selenium, Stibnite cells do not regain their original conductivity immediately at the end of an exposure, but require time. Compared with Selenium, however, this return is much more rapid.

Stibnite at the Temperature of Liquid Air:-

Sensibility curves were obtained at this temperature and the law connecting galvanometer deflections and energy investigated. No statement need be made of the method of procedure as it was identical with that used for Selenium. As it was proposed to use an exposure of ten seconds for the sensibility curves at this temperature, the law connecting energy and deflection was investigated under these conditions and this value used in reducing the galvanometer deflections to equal energies. The data referring to this part of the work follows:

Stibnite Cell "D" Temperature - 190°C.
Voltage 120 10 secs. exposure.

Wave-lengths	D_1 = Galv.Defl. full energy	D_2 = Galv.defl. Half energy	β calc. from D_1 and D_2
.577 μ	13.65 mm.	8.3 mm.	.71
.616	17.25	10.14	.74
.735	21.6	12	.85
.813	30.9	17.97	.78
		Mean Value	.77

Sensibility Curves - 190° C. Stibnite.

A number of experiments were carried out on different cells. The data and curves will be given for but one cell, Stibnite "C". This cell was of the scratched cleavage surface variety and had a slightly lower conductivity than cell Stibnite "D". Unfortunately this cell burned out before its resistance was accurately determined.

Table VIII.

Stibnite Cell "C". Temperature - 190° C.
120 Volts. 10 sec. exposure.

Wave-length	Energy Defl.	Galv. Defl.	Δc_1 calc. E=48mm β=.5	Δc_2 calc. e=48mm β=1.	Δc_3 calc. E=48mm β =.77
.520μ	8 mm	4 mm	9.8mm	24mm	18.22
.550	19	5.5	8.7	10.10	11.23
.580	35	6.0	7.1	8.22	7.66
.600	51	13.	12.61	12.24	12.41
.620	46	14.	14.3	14.61	14.46
.632	46	11.5	11.8	12.	11.88
.642	49	19.	18.8	18.61	18.70
.649	49	33.	32.7	32.32	32.48
.655	52	80.	76.9	73.85	75.22
.660	48	232	232	232	232
.665	13	240	461.2	890.35	656.21
.670	3.75	214	765.6	2739	1523.93
.678	1	197	1333.79	9456.	3881.67
.685	1.2	180	1311.09	7200.	3082.20
.692	1.5	77.5	438.10	3121.4	1117.50
.700	9.0	152.0	409.20	810.6	551.6
.710	16.0	143.0	247.68	429.0	333.2
.730	19.0	131.0	208.21	330.9	267.4
.751	22.0	141.0	208.27	307.6	257.1
.773	26.0	152.0	206.53	276.1	243.6
.800	31	164.	204.08	253.9	235
.825	33	177.	213.48	257.5	236.2
.850	39	185 .	205.14	227.7	217.1
.880	43.5	194.	202.79	214.1	209.3
.930	45	184	190.04	196.3	193.4
.982	37	150	170.85	194.6	175.1
1.080	43	125	132.06	139.5	136.1
1.190	48	79	79	79	79
1.348	43	33	34.86	36.84	35.91
1.62	46	6	6.13	6.2	6.2
1.92	46	0	0	0	0

Curve VIII gives the results in a curve. The value of β used in reducing the deflections to equal energies was .77. It is to be noticed, however, that while the value of the ordinates depends upon the ~~power of~~ exponent assumed, there would be no shift of the posi-

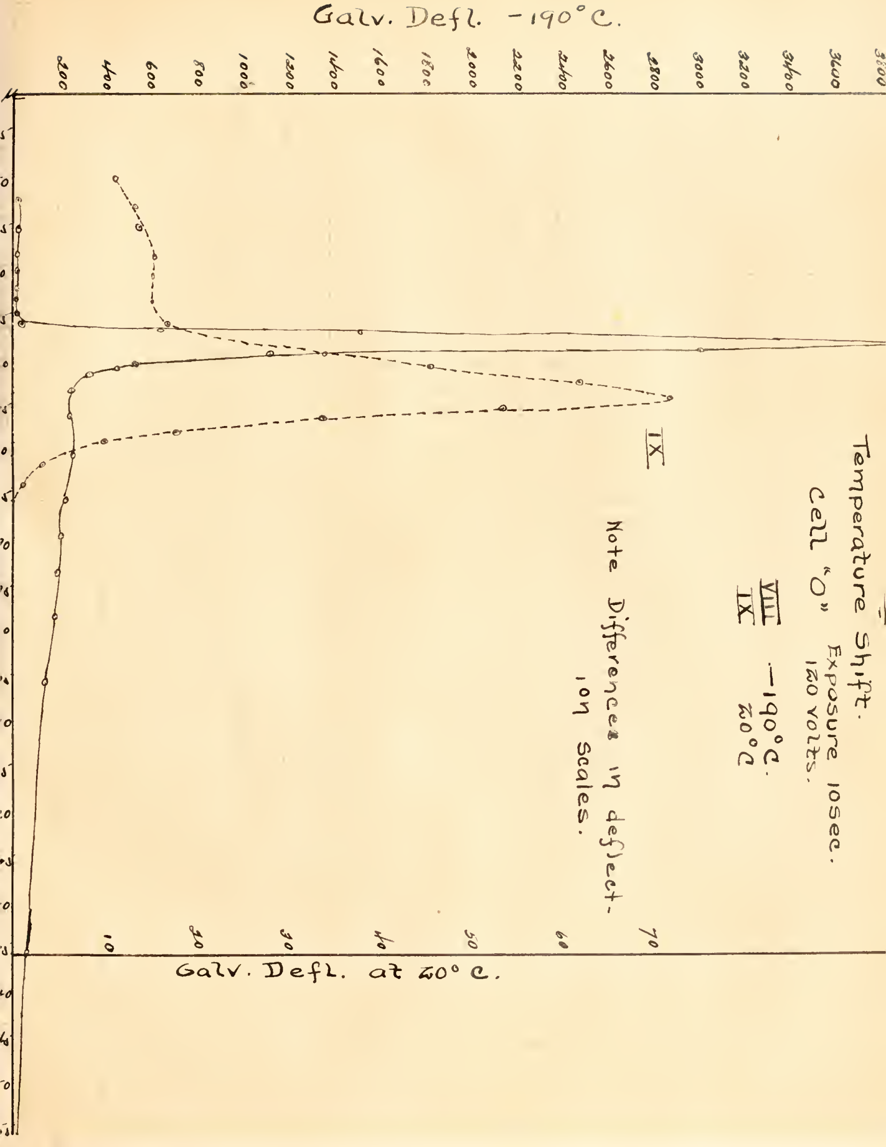
tion of the maximum for values of β ranging from .5 to 1.

For purposes of comparison there are given at this point the sensibility data for the same cell at room temperature.

Table IX.

Stibnite O. 20° C.
10 Volts. 10 sec. exposure.

Wave-length	Energy Defl.	Galv. Defl.	Δc calc. E = 48 mm. β = .5
.495 μ	12 mm.	5.5 mm.	11 mm.
.520	17	8	13.44
.535	25	10	13.86
.550	36	13.5	15.59
.565	38.5	14.5	16.19
.580	52.	17.	16.33
.600	51	16	15.58
.620	48	13.5	13.5
.642	48	15.5	15.5
.670	46	16.5	16.85
.696	46	31	31.67
.705	47	46	46.49
.720	46	61	62.31
.735	50	71.8	70.35
.742	52	75	72.06
.751	48	54.3	54.3
.762	48	34.5	34.5
.774	48	18.25	18.25
.785	47	10.5	10.61
.813	49	3	2.97
.837	47	1	1.01


Galv. Defl. -190°C.
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
Temperature Shift.
Cell "O" Exposure 10 sec.
120 volts.
VIII -190°C.
IX 20°C
IX
Note Differences in deflection Scales.
10
20
30
40
50
60
70
Galv. Defl. at 20° C.

From a comparison of Curves IX and X these two conclusions stand out most prominently: Lowering the temperature of Stibnite from 20° to - 190°C. causes:

1. Extension of region of sensibility to 2μ approximately.

2. Shift of approximately 600 A.U. of the sensibility maximum towards the region of shorter wave-lengths. This is what was also found for Selenium.

Anomalous Stibnite Cells:-

In addition to the general characteristics enumerated above, two cells "Stibnite B" and "Stibnite X" exhibited surprising properties. A preliminary test with an incandescent lamp indicated that these cells were quite normal, but with monochromatic light some unexpected properties were found. For certain regions of the spectrum these cells were photo-negative while for the longer wave-lengths they were photo-positive. The performance of "Stibnite B" taken at room temperature is given in Table XI on following page.

Table XI.

Stibnite "B" Temperature $20^\circ.5$ C.

20 Volts. 10 sec. Exposure.

Wave-lengths	E_1=Energy Defl.	D_1 =Galv. Defl.	E_2=Energy Defl.	D_2= Galv. Defl.
.5035 μ	11.5 mm.	-8 mm.	2.0 mm.	-5 mm.
.5302	20.5	-10	3.25	-5
.5602	40	- 7.5	7	-7
.5936	79	-10	14.5	-7.4
.634	160.5	- 5.2	31	-5
.657	219	0	47.5	0
.695	229	+16mm.	54	+9
.724	234	+18	57.5	+10.5
.767	198	+19.5	54.5	+4
.806	185			

It seems well to mention that whenever the deflection was negative an additional negative deflection was observed immediately at the end of the exposure. Just what the explanation is it is impossible to say, but it is certain that the effect is in the cell itself and not due to external electrical influences. From a glance at the table, it is seen that no deflection is recorded for λ=.657μ. The inference must not be drawn from this that the galvanometer needle remained entirely quiescent. As a matter of fact there was first a positive deflection of 1.5 mm. followed immediately by an equal negative deflection. An attempt was made to find the law for the cell connecting energy and deflection. No simple relation was found. It is evident that we are dealing here with the superposition

of two effects. A superficial study shows that if the law $D = K E^{\beta}$ does apply, the values of β for negative and positive deflections are entirely different.

At the temperature of liquid air this cell showed the maximum in the usual position. At this temperature, the negative effect was entirely absent. The range of sensibility had been extended considerably, positive deflections being recorded from .48μ to 2.5 μ . Returning to 20°C, the cell was found to be light negative again. The writer hopes to investigate photo-negative Selenium prepared according to Brown's process, to see whether or not this photo-negative property is fundamental in character.

Cell "Stibnite X" when first prepared, showed this photo-negative property even more striking than "Stibnite B". Twenty-four hours later this had entirely disappeared and the cell though normal was now very unsteady. The transient character of this photo-negative property as indicated by "Stibnite X" is controvented by cell "Stibnite B" (fully described above). At the time of writing "Stibnite B" which is a month old, still retains its photo-negative characteristics. Further studies on these so-called anomalous Stibnite cells are to be made with a more rapidly moving galvanometer.

Oxides of Copper, Nickel, Iron and Molybdenite.

Oxides of copper, nickel and iron were prepared in cell form. These together with molybdenite were investigated in a superficial manner with light from an incandescent bulb. While these gave indications of light sensitiveness, I am not prepared to say just how much of the deflection was due to pure heating. The full investigation of this point had to be postponed as the quantities involved were of such a different order of magnitude that a complete re-arrangement of apparatus would be required.

Theoretical Discussion:

More extended experimental data must be at hand before a theoretical discussion becomes profitable. It would not be surprising, however, to find some connection between these results and the optical properties. It will be remembered that Pfund[1] found the sensibility maximum of Selenium to lie in the region of increasing transparency. Nicholson's[2] experiments have a bearing in this connection. Königsberger[3] and Müller[4] have

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[1] Pfund. Phys. Rev. XXVIII, No. 5, 1909.
[2] Nicholson. Phys. Rev. Vol. III, No. 1, 1914.
[3] Koenigsberger. Ann d. Phys. Band 43, heft 8, p. 1205, 1914.
[4] Mueller. N. J. F. Min. Blbd. 17, 244, 1903.

found for Stibnite an increasing transparency at the edge of the visible spectrum, and Trowbridge[1] found a temperature shift of the transparency maximum of molybdenite of about the same magnitude as found in these experiments for the sensibility maximum. It might be mentioned in passing that certain experiments performed on the transparency of a cathode film of Stibnite at 20° and -190° C. indicate a slight shift of the transparency, although the evidence is far from satisfactory.

Summary:

To summarize the results of this paper:

1. A new form of Selenium cell has been prepared which does not crack at the temperature of liquid air.
2. Sensibility curves of Selenium and Stibnite at 20° C and - 190° show that the low temperature causes:
    (a) A shift of the maximum sensibility towards the region of shorter wave-lengths by about 600 A.U. for both Stibnite and Selenium.
    (b) An extension of the range of sensibility from .9μ to 2 μ.

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[1] Trowbridge. Phys. Rev. Vol. II, No. 5, Nov. 1905.

3. Sensibility curves for Stibnite for 20 and 120 volts at 20° C. show a slight apparent shift to shorter wave-lengths for the higher voltage. This shift, if it has a true existence, is of a different order of magnitude from the temperature shift.

4. Sensibility curves for the same Stibnite cell ~~of~~ for both equilibrium exposure~~s~~ and exposures of ten seconds show a shift towards longer wave-lengths for the equilibrium exposure.

5. Investigation of law connecting deflections and energy for Stibnite shows:

   a. At 20°C. Stibnite obeys square root law, i.e.

   $$D = K\,E^{\beta} \text{ where } \beta = .5.$$

   b. At - 190°C. for exposures of 10 secs. $\beta = .77$.

6. Stibnite shows voltage effects.

7. Certain oxides and molybdenite give promise of a photo-electric effect.

Conclusions: -

1. Both Selenium and Stibnite obey the law $D = K\,E^{\beta}$ at 20°C. When equilibrium condition has been established, $\beta = .5$.

2. Both substances show the voltage effects, confirming the results of Ries and others.

3. Both Selenium and Stibnite experience a very great extension of the range of sensibility into the infra-red when cooled down to the temperature of liquid air.

4. Lowering the temperature from 20° C. to - 190° C. causes the sensibility maximum for both Selenium and Stibnite to shift to the region of shorter wave-lengths by about 600 A. U.

5. These results would seem to indicate that the mechanism which brings about light sensitiveness in Selenium and Stibnite is of the same general character.

In conclusion I wish to thank Professor J. S. Ames for suggesting the problem and for his interest throughout the investigation. To Professor Pfund for his many helpful suggestions and for his constant encouragement I wish to express my sincere appreciation.

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Vita.

Daniel Stanley Elliott, son of George Herbert and Minnie Prinz Elliott, was born in Baltimore, Md. August 3, 1885. After a preliminary education in the public schools, followed by three years in the Government Postal Service, he matriculated at the Johns Hopkins University in 1907. He received the degree of Bachelor of Arts in 1911, and the following year enrolled as a graduate student in Physics. He was admitted to the degree of Master of Arts in 1913, and held the Fellowship in Physics in 1913-1914. Since his enrollment as a graduate student he has pursued courses in Physics, Astronomy and Mathematics under Professor Ames, Associate Professor Anderson and Dr. Cohen.

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